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(54) Title: IONIC LIQUIDS (57) Abstract <p>This invention relates to an ionic liquid comprising a dialkyl substituted imidazolium halide wherein at least one of the said alkyl substituents has 6 or more carbon atoms, a method of preparation of such imidazolium halides, and the use thereof for hydrocarbon conversion reactions such as oligomerization or polymerization of olefins and for the alkylation of paraffins, isoparaffins or aromatics with olefins. Polymerization of C4 raffinates using these ionic liquids as catalysts enables a much higher percentage of n-butenes to be incorporated in the product polymer than would be possible in conventional cationic polymerization processes.</p>		

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IONIC LIQUIDS

This invention relates to novel ionic liquids and to the use thereof as the reaction medium and catalyst for various chemical reaction such as eg producing olefin polymers, especially butene polymers from raffinates I and II from a refining process and which
5 contain *inter alia* a mixture of butene-1, butene-2 and iso-butene.

Ionic liquids are primarily mixtures of salts which melt below room temperature. Such salt mixtures include aluminium halides in combination with one or more of imidazolium halides, pyridinium
10 halides or phosphonium halides and the latter being preferably substituted. Examples of the latter include one or more of 1-methyl-3-butyl imidazolium halides, 1-butyl pyridinium halide and tetrabutyl phosphonium halides.

It is known to use these ionic liquids as solvents and as catalysts for eg the dimerization and /or oligomerization of olefins
15 such as ethylene, propylene, butene-1 and/or butene-2 and for the alkylation of benzene using alkyl halides. In this context Jeffrey A Boon et al states in an article in the Journal of Organic Chemistry, Vol 51, 1986, pp 480-483 that:

"Completely ionic liquids are not the usual solvent for organic
20 reactions. Most ionic liquids are liquid only at high temperatures and offer little advantage over the more commonly used aqueous or organic media. Most work on organic reactions in molten salts have employed eutectic mixtures, but they still require temperatures above 200°C."

25 This article further goes on to state that:

"Numerous other substituted imidazolium and pyridinium chlorides form molten salts with aluminium chloride but do not possess the favourable physical properties we sought for this investigation."

5 From the above, it is clear that not all ionic liquids possess the properties desirable for specific reactions in which they are to be used and that the choice of specific ionic liquids for a given reaction is far from straightforward.

10 A further article by Yves Chauvin et al in J Chem Soc, Chem Comm, 1990, pp 1715-1716 also emphasises this point. In this article, the authors intend to carry out catalytic dimerization of alkenes by nickel complexes in organochloroaluminate molten salts to the exclusion of all other products. Moreover, the authors state that:

15 "However, it seems that no attempt has been made to take advantage of the solubility of the organometallic catalyst and the insolubility of the reaction products of the catalytic reaction in these solvents."

The authors add that:

20 "In the absence of any nickel complex, acidic melts catalyse the formation of oligomers, the molecular weight of which is characteristic of a cationic reaction".

To further add to the unpredictability of these reactions, FR-A-2611700 (Institut Francais du Petrole) describes a process for
25 the oligomerization of olefins including *inter alia* butene-1 and butene-2 using a nickel catalyst in the liquid phase; the catalyst used is specifically a nickel complex dissolved in an ionic liquid, the latter being the liquid phase.

30 More recently, FR-A-2626572 describes a process for alkylation using as catalyst an ionic liquid comprising at least one halide of aluminium or boron and at least one quaternary ammonium halide. The quaternary ammonium halide can be a dialkylimidazolium halide in which one of the alkyl substituents can be an amyl group, ie it has 5 carbon atoms.

35 From the above it will be clear that the function of ionic

liquids in these reactions is far from predictable. Furthermore, none of the publications referred to above disclose ionic liquids comprising alkyl substituted imidazolium halides in which any of the alkyl substituents has more than 5 carbon atoms.

5 It has now been found that ionic liquids comprising alkyl imidazolium compounds in which the alkyl substituent has 6 or more carbon atoms have remarkable properties.

Accordingly, the present invention is an ionic liquid comprising a dialkyl substituted imidazolium halide wherein at least
10 one of the said alkyl substituents has 6 or more carbon atoms.

It is well established that imidazolium compounds when used in ionic liquids contain at least two alkyl groups substituted in the 1- and the 3-positions of the imidazolium structure. The substituents in these two positions are, by and large interchangeable. Thus, in
15 the imidazolium halides of the present invention, at least one of the substituents in the 1- or the 3-position is an alkyl group having at least 6 carbon atoms. The precise position of each is immaterial since such 1,3-disubstituted imidazolium halide is a symmetrical molecule. This alkyl substituent having 6 or more carbon atoms can
20 be a straight chain alkyl group or a branched chain alkyl group. These alkyl groups suitably contain from 6-30 carbon atoms, preferably from 6-18 carbon atoms.

The halide group in the imidazolium compounds of the present invention may be a chloride, a bromide or an iodide group.

25 Specific examples of imidazolium compounds present in the ionic liquids include:

1-methyl-3-hexyl-imidazolium chloride
1-methyl-3-octyl-imidazolium chloride
1-methyl-3-decyl-imidazolium chloride
30 1-methyl-3-dodecyl-imidazolium chloride
1-methyl-3-hexadecyl-imidazolium chloride
1-methyl-3-octadecyl-imidazolium chloride.

As will be appreciated, in the above listed compounds it would be possible to substitute any other C1-C4 alkyl group such as an
35 ethyl, propyl, isopropyl, butyl, isobutyl or a tert-butyl group

instead of the methyl group in the 1-position in order to achieve the same effect. As explained above, it would be possible to interchange the position of the substituents in the 1- and 3- positions or to have each of the substituents in the 1- and 3- positions with 5 or more carbon atoms in the alkyl group since the 1,3-disubstituted imidazolium halide is a symmetrical molecule. Furthermore, it would also be possible to have the chloride ion in the compounds listed above interchanged with bromide or iodide ions to produce compounds which are equally effective as ionic liquids.

10 The imidazolium halides of the present invention can be prepared by the following method:

For instance, a 1-methyl-3-(C6+)alkyl imidazolium halide (wherein "C6+" represents 6 or more carbon atoms) can be prepared by mixing dry 1-methylimidazole with 1-(C6+)alkyl haloalkane (and optionally with a solvent such as eg acetonitrile, if a homogeneous mixture is desired) and placing them eg in a Corius tube inside a dry box. The Corius tube is then closed using a super seal in the dry box and sealed under vacuum. The two components form two layers inside the Corius tube and the resulting mixture is then heated to about 90°C for about a week. The resultant product is then cooled to room temperature to form a viscous product which is then transferred from the dry box to a Schlenk round bottomed flask and left under vacuum for a few hours. The resultant viscous liquid is then purified by recrystallisation from acetonitrile and analysed for identification and characterisation of the 1-methyl-3-(C6+)alkyl imidazolium halide.

A feature of the present invention is that where the chain length of at least one of the alkyl chains in the dialkyl imidazolium halide is greater than 5 carbon atoms, the catalytic activity of ionic liquids comprising such halides is increased for polymerization reactions with respect to alkyl chains having 4 carbon atoms or less. The performance of such ionic liquids is particularly superior when the feedstock being polymerised is a raffinate I, raffinate II or isobutene.

35 A further feature of the present invention is that the polymers

produced using ionic liquids comprising the dialkyl imidazolium halides of the present invention can, if desired, have a higher molecular weight distribution than those obtained containing conventional imidazolium halides.

5 The ionic liquids of the present invention suitably contain in addition to the dialkyl imidazolium halides defined above an aluminium compound which is suitably an aluminium halide, such a aluminium trichloride or an alkyl aluminium halide such an alkyl aluminium dichloride or a dialkyl aluminium halide and is preferably
10 ethyl aluminium dichloride.

It is well understood in the art that the ratio of the components in an ionic liquid used as catalyst should be such that they remain in a liquid state under the reaction conditions. A yet another feature of the present invention is that when preparing
15 multi-component ionic liquids, the presence of the dialkyl imidazolium halides of the present invention enables such liquids to tolerate a higher proportion of the other component(s) and still remain liquids, in some cases at room temperature, than is possible with conventional imidazolium halides.

20 Ionic liquids produced from imidazolium halides of the present invention can be used as catalysts for any of the reactions in which ionic liquids have conventionally been used. Such reactions include oligomerization, alkylation, polymerization and the like. In particular, ionic liquids comprising the dialkyl imidazolium halides
25 of the present invention are particularly suitable for the oligomerization and polymerization of olefins, especially feedstock comprising isobutenes.

Thus, according to a further embodiment, the present invention is a process for the polymerization of an olefinic feedstock
30 comprising one or more of C2-C4 olefins, said process comprising bringing the feedstock into contact with an ionic liquid comprising

- a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2, and
- 35 b) a dialkyl substituted imidazolium halide in which at least one

of the alkyl substituents has six (6) or more carbon atoms such that the melting point of the ionic liquid is below the reaction temperature.

The polymerization products referred to herein are meant to include:

- i. oligomers which are conventionally defined as "a very low molecular weight polymer in which the number of repeating units equals 2-10" (see Polymer Chemistry, An Introduction by R B Seymour and C E Carraher, 2nd Edition, 1988, p 14, and published by Marcel Dekker Inc), and
- ii. polymers which have at least 11 repeating units, ie an average molecular weight of 600 to 100,000.

The hydrocarbon feedstock for this process is suitably ethylene, propylene, butene-1, butene-2 and/or isobutene but is preferably a raffinate from the refining process and can be raffinate I or raffinate II.

Raffinate I is usually the butadiene raffinate which is a by-product formed during the thermal or catalytic cracking (whether or not fluid) operation in a refinery and principally comprises C4 hydrocarbons especially a mixture of butene-1, butene-2 and iso-butene along with some saturated hydrocarbons. More specifically, such raffinate I comprises at least 10% w/w of iso-butene, from 20-40% w/w of butene-1 and butene-2, and from 10-20% w/w of butanes.

Raffinate II is the unpolymerised by-products recoverable when Raffinate I is subjected to polymerization using eg Lewis acid catalysts or the by-product gases resulting from the production of the lead-free anti-knock compound, methyl tertiary butyl ether (MTBE). In both processes the by-products have substantially the same composition and are rich in n-butenes. These by-products are the so called "raffinate II" and typically contain from 30-55% w/w of butene-1, about 10% w/w of cis-butene-2, about 17% w/w of trans-butene-2, upto 6% w/w of iso-butene and upto 30% w/w of the saturated C4 hydrocarbons n-butane and iso-butane. Since raffinate II, an otherwise wasted material, is capable of being cationically polymerized to polybutenes, its value as raw material is readily

apparent.

The ionic liquids that can be used comprise an aluminium or gallium compound which is suitably a halide, such as aluminium trichloride or gallium trichloride, or, an alkyl aluminium/gallium halide such as an alkyl aluminium/gallium dichloride or a dialkyl aluminium/gallium chloride and is preferably ethyl aluminium/gallium dichloride. The component (b) in the ionic liquid is a dialkyl substituted imidazolium halide, especially the 1-(C1-C4)alkyl-3-(C6+)alkyl-imidazolium halides of the present invention described above. Of the alkyl imidazolium halides listed above, 1-methyl-3-octylimidazolium chloride is preferred.

The relative ratios of the two components (a) and (b) in the ionic liquid should be such that they are capable of remaining in the liquid state under the reaction conditions. Typically, the relative mole ratio of aluminium/gallium compound to the component (b) in the ionic liquid is suitably in the range from 1 : 2 to 3 : 1, preferably from 1.5 : 1 to 2 : 1. Within this range, where the ionic liquid is intended for use as a reaction medium or a solvent, the amount of the component (a) can be less than 50 mole % of the total ionic liquid. However, where the ionic liquid is intended for use as a catalyst, the amount of component (a) is preferably greater than 50 mole % of the total ionic liquid.

The polymerization reaction is suitably carried out at a temperature from -50°C to +100°C, preferably from -30°C to +70°C. The reaction can be carried out either:

- (i) by bubbling the olefinic hydrocarbon feedstock to be polymerized through the ionic liquid, or,
- (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and then subjecting such a dispersion to polymerization.

In the case of (i), the rate at which the olefinic hydrocarbon feedstock is to be bubbled and in the case of (ii), the amount of ionic liquid mixed with the feedstock and, in both cases the reaction temperature used will depend upon the molecular weight of the product desired. Normally in this type of reaction one would expect that the

higher the temperature used, the lower the molecular weight of the polymer formed.

It has now been found that , surprisingly, when the process (i) is used, the polymer product forms a separate layer and floats on the surface of the ionic liquid. This product layer is substantially free of any catalyst or ionic liquid contaminants. The polymer product can thus be readily removed from the ionic liquid surface eg by tapping. This feature has several advantages:

- A. Ease of separation of the product polymer from the catalytic component means that further reaction of the olefinic end-group in the polymer, such as eg isomerization, is minimised thereby retaining the structure of the polymer formed. This means that such further undesirable reactions are avoided without resort to the use of conventional reaction quenching agents such as aqueous alkali.
- B. The polymer product formed need not be water-washed because of the relatively low levels of the catalytic ionic liquid in the product thereby avoiding a process step.

If process (ii) is used, it may be necessary to add a quenchant such as aqueous ammonia in order to terminate the reaction and/or to neutralise any catalytic components. The products can then be water-washed and the product polymer separated. In this case, the unreacted material can be allowed to evaporate and the dried product isolated.

A further feature of the present invention is that this method enables a much higher percentage of n-butenes to be incorporated in the product polymer than would be possible in conventional cationic polymerization processes using eg aluminium trichloride or boron trifluoride.

Yet another surprising feature of the present process is that contrary to expectations, the molecular weight of the product does not increase with decreasing reaction temperatures. In spite of using reaction temperatures which are substantially higher than those used in the prior art, the present process gives rise to polymers which have a higher molecular weight than the oligomers formed by said prior art processes.

These surprising features give a very desirable outlet for relatively low value feedstocks such as raffinates I and II at the same time making maximum use of the reactive carbon values in that feedstock and hence reducing the wastage of any hydrocarbon values in such feedstock.

The polymer products produced by the process of the present invention can be used eg as lubricants or cutting fluids in the industry without further treatment. Alternatively, these polymers can be maleinised and converted to corresponding succinic anhydride derivatives which in turn can be converted into the corresponding imide which is a detergent for lube oils and fuels.

As mentioned previously, the ionic liquids of the present invention can also be used eg for alkylation reactions.

Where these ionic liquids are used as catalysts for the alkylation reaction, this may be either the alkylation of isoparaffins such as isobutane with a C2-C4 olefin such as eg ethylene, to produce alkylates which enhance the octane rating of fuels, or, for the alkylation of aromatics with an olefins such as eg the conversion of benzene to ethyl benzene with a view to producing styrene therefrom. The alkylation reaction is suitably carried out at a temperature of eg below 100°C, suitably from -30 to +50°C. The ratio of the catalytic ionic liquid phase to the hydrocarbon phase used for alkylation would largely depend upon the reactivity of the olefin and the acidity of the particular ionic liquids chosen. As a general guide the mole ratio of catalyst to olefins is suitably in the range from 1000 : 1 to 1 : 1000. In terms of the volume ratio of catalyst phase to hydrocarbon phase, this would suitably be in the range from in the range from 100 : 1 to 1 : 100, and more preferably from 20 : 1 to 1 : 20.

Where an iso-paraffin is being alkylated with an olefin, the ratio of iso-paraffins to olefin is suitably in the range from 1000 : 1 to 1 : 1000.

The present invention is further illustrated with reference to the following Examples. In all the Examples, the 1-methylimidazole used was distilled over sodium hydroxide and was always handled under

a cover of nitrogen. The alkyl halides used were all dried over calcium hydride for a week and then distilled prior to use.

It is not believed that any detailed analysis of these compounds is necessary in order to ascertain their structure since the reactions are stoichiometric, no gases are evolved nor any solids deposited during the reaction. However, in order to prove that this is the case, ^1H NMR analyses has been carried out on the products from some of the Examples and on this basis a structure has been assigned for those products on which no NMR analyses have been carried out.

10 In Tables below, the intensity referred to is the peak height which corresponds to the number of protons in that position. In this respect the notations very strong, strong, medium and weak represent the following range of peak intensities (I/I_0):

very strong	-	80-100
15 strong	-	60-80
medium	-	40-60
weak	-	20-40
very weak	-	<20
$\delta(\text{ppm})$	-	chemical shift in parts per million

20 EXAMPLE 1: Preparation of 1-hexyl-3-methyl Imidazolium Chloride:

Dry 1-methylimidazole (9.03 g, 0.11 mol) was mixed with 1-chlorohexane (12.06 g, 0.1 mol) and placed in a Corius tube inside a dry box. The Corius tube was then closed using a super seal in the dry box and sealed under vacuum. The two components formed two layers, inside the Corius tube, and this mixture was heated at 100°C for a week. The resulting product was allowed to cool to room temperature when it formed a viscous product. The viscous product was transferred from the dry box to a Schlenk round bottomed flask where it was left under vacuum for 4 hours to form a viscous liquid. 25 The product was the ionic liquid 1-hexyl-3-methyl imidazolium chloride at room temperature and the yield was 12.23 g (92.2%) with an m/z value of 369.

EXAMPLE 2: Preparation of 1-octyl-3-methyl Imidazolium Chloride:

The process of Example 1 above was repeated except that 1-chlorooctane (14.9 g, 0.1 mol) was used instead of 1-chlorohexane. 35

The product was the ionic liquid 1-octyl-3-methyl imidazolium chloride at room temperature, the yield was 15.8 g (96.6%) and had an m/z value of 425.

EXAMPLE 3: Preparation of 1-nonyl-3-methyl Imidazolium Chloride:

5 The process of Example 1 was repeated except that 1-chlorononane (16.3 g, 0.1 mol) was used instead of 1-chlorohexane. The product was the ionic liquid 1-nonyl-3-methyl imidazolium chloride at room temperature, the yield was 16.1 g (90.0%) and had an m/z value of 453.

10 **EXAMPLE 4: Preparation of 1-decyl-3-methyl Imidazolium Chloride:**

 The process of Example 1 was repeated except that 1-chlorodecane (17.7 g, 0.1 mol) was used instead of 1-chlorohexane. The product was the ionic liquid 1-decyl-3-methyl imidazolium chloride at room temperature, the yield was 18.3 g (94.2%) and had an m/z value of 481.

EXAMPLE 5: Preparation of 1-dodecyl-3-methyl Imidazolium Chloride:

 The process of Example 1 was repeated except that 1-chlorododecane (20.48g 0.1 mol) was used instead of 1-chlorohexane. The product upon heating at 100°C was waxy and was recrystallised from acetonitrile (50 ml) at -13°C for a week in a Schlenk round bottomed flask. The crystals were isolated by Schlenk filtration and dried *in vacuo* for 48 hours. The ^1H NMR analysis of the crystals is shown in Table 1 below. The crystals had a melting point of 52.5 °C, the yield was 19.4 g (86.1%) and had an m/z value of 537.

25

30

35

TABLE 1
C₁/C₁₂ Melt NMR of a Product containing 40 mole % of AlCl₃
(Example 5)

δ (ppm)	Intensity (I/I ₀)	Type
0.5	weak	singlet
0.9	very strong	doublet
1.5	very weak	singlet
3.5	weak	singlet
3.8	very weak	singlet
4.6	very weak	singlet
5.3	very weak	singlet
7.0	very weak	singlet
8.0	very weak	singlet

5 **EXAMPLE 6: Preparation of 1-tetradecyl-3-methyl Imidazolium Chloride:**

The process of Example 5 was repeated except that 1-chlorotetradecane (23.3 g 0.1 mol) was used instead of 1-chlorododecane. The crystals formed were not analysed by ¹H NMR but were assigned the structure 1-tetradecyl-3-methyl imidazolium chloride by analogy with Example 5. The crystals had a melting point of 56.89°C, the yield was 23.9 g (93.3%) and had an m/z value of 593.

10 **EXAMPLE 7: Preparation of 1-hexadecyl-3-methyl Imidazolium Chloride:**

The process of Example 5 was repeated except that 1-chlorohexadecane (26.09 g 0.1 mol) was used instead of 1-chlorododecane. The crystals were not analysed by ¹H NMR but were assigned the structure 1-hexadecyl-3-methyl imidazolium chloride by analogy with Example 5. The crystals had a melting point of 61.6°C, the yield was 25.7 g (89.6%) and had an m/z value of 649.

20 **EXAMPLE 8: Preparation of 1-octadecyl-3-methyl Imidazolium Chloride:**

The process of Example 5 was repeated except that 1-chlorooctadecane (28.9 g 0.1 mol) was used instead of 1-chlorododecane. The crystals were not analysed by ¹H NMR but the structure was assigned as 1-octadecyl-3-methyl imidazolium chloride on the basis of analogy with Example 5. The crystals had a melting

point of 71.07°C, the yield was 31.77 g (93.3%) and had an m/z value of 705.

EXAMPLE 9:

5 An ionic liquid was prepared using 1-methyl-3-octyl imidazolium chloride and aluminium trichloride in a mole ratio of 2:1 as described in Example 2 above. 5ml of the ionic liquid so formed was dispersed into 200g of raffinate II feedstock (having an olefinic content of 62% w/w and a composition shown in Table 2 below) in 750 ml of heptane with stirring at atmospheric pressure and at 10°C for a
10 duration of 180 minutes. The reaction was exothermic but a temperature rise of no greater than 10°C was observed during the reaction period. The yield of the polymer product was 76.8% wt/wt based on the weight of olefin present, ie 95.3 g of polymer product was obtained from 124.0g of olefin. The number average molecular
15 weight of the polymer, M_n , was 1042.

TABLE 2

Raffinate II Feedstock Olefin	% wt/wt Concentration
Iso-butene	1.0
Butene-1	35.0
Trans-butene-2	20.0
Cis-butene-2	6.0
Saturated hydrocarbons	remainder

20

25

Claims:

1. An ionic liquid comprising a dialkyl substituted imidazolium halide wherein at least one of the said alkyl substituents has 6 or more carbon atoms.
2. An ionic liquid according to Claim 1 wherein the alkyl
5 substituent having 6 or more carbon atoms is a straight chain alkyl group or a branched chain alkyl group.
3. An ionic liquid according to Claim 1 or 2 wherein the alkyl substituent having 6 or more carbon atoms has from 6-30 carbon atoms.
4. An ionic liquid according to any one of the preceding Claims
10 wherein the halide group in the imidazolium halide is a chloride, a bromide or an iodide group.
5. An ionic liquid according to any one of the preceding Claims wherein the imidazolium halide is selected from the group consisting of:
15 1-methyl-3-hexyl-imidazolium chloride
1-methyl-3-octyl-imidazolium chloride
1-methyl-3-decyl-imidazolium chloride
1-methyl-3-dodecyl-imidazolium chloride
1-methyl-3-hexadecyl-imidazolium chloride
20 1-methyl-3-octadecyl-imidazolium chloride.
6. An ionic liquid according to Claim 5 wherein the 1-methyl group in each of the compounds is replaced by a C2-C4 alkyl group.
7. An ionic liquid according to Claim 6 wherein the C2-C4 alkyl group is selected from the group consisting of: an ethyl, propyl,
25 isopropyl, butyl, isobutyl or a tert-butyl group

8. An ionic liquid according to any one of Claims 5-7 wherein the chloride ion in the compounds listed above is interchanged with bromide or iodide ions.
9. A process for producing ionic liquids according to Claim 1
5 wherein a dialkyl imidazolium halide is prepared by mixing dry 1-(C1-C4)alkyl imidazole with 1-(C6+)alkyl haloalkane, optionally with a non-aqueous solvent, the temperature of the mixture is elevated, the mixture maintained at this elevated temperature for a duration, then cooled and the desired ionic liquid is recovered as such or
10 optionally after purification by recrystallisation.
10. An ionic liquid according to any one of the preceding Claims 1-8 wherein said ionic liquid contains in addition to the dialkyl imidazolium halide, an aluminium compound which is selected from an aluminium halide, an alkyl aluminium halide or a dialkyl aluminium
15 halide.
11. An ionic liquid according to Claim 10 wherein the ratio of the dialkyl imidazolium halide to the aluminium compound is such that when used as a catalyst they remain in a liquid state under the reaction conditions under which the catalyst is used.
- 20 12. A process for the conversion of olefinic hydrocarbons said process being selected from the group consisting of oligomerization, alkylation and polymerization in the presence of an ionic liquid and wherein the ionic liquid comprises a dialkyl imidazolium halide according to any one of the preceding Claims 1-8 and 10-11.
- 25 13. A process according to Claim 12 wherein the olefinic hydrocarbon comprises one or more of C2-C4 olefins.
14. A process according to Claim 12 or 13 wherein the olefinic hydrocarbon feedstock comprises ethylene, propylene, butene-1, butene-2 and/or isobutene.
- 30 15. A process according to Claim 12 or 13 wherein the olefinic hydrocarbon feedstock is a raffinate from a refinery process selected from raffinate I or raffinate II.
16. A process according any one of the prededing Claims 12-15, said process comprising polymerization of an olefinic hydrocarbon
35 feedstock comprising the olefinic hydrocarbon into contact with an

ionic liquid comprising

- a) a compound of the formula R_nMX_{3-n} wherein R is a C1-C6 alkyl radical, M is aluminium or gallium, X is a halogen atom and n is 0, 1 or 2, and
 - 5 b) a dialkyl substituted imidazolium halide in which at least one of the alkyl substituents has six (6) or more carbon atoms such that the melting point of the ionic liquid is below the reaction temperature.
17. A process according to Claim 16 wherein the relative ratios of
- 10 components (a) and (b) in the ionic liquid is in the range from 1 : 2 to 3 : 1.
18. A process according to Claim 16 or 17 wherein the polymerization products comprise:
- i. oligomers which are conventionally defined as "a very low
 - 15 molecular weight polymer in which the number of repeating units equals 2-10" and
 - ii. polymers which have at least 11 repeating units, ie an average molecular weight of 600 to 100,000.
19. A process according to any one of the preceding Claims 12-18
- 20 wherein the polymerization reaction is carried out at a temperature from -50°C to +100°C.
20. A process according to any one of the preceding Claims 12-19 wherein the polymerization reaction is carried out either:
- (i) by bubbling the olefinic hydrocarbon feedstock to be
 - 25 polymerized through the ionic liquid, or,
 - (ii) by dispersing the ionic liquid in appropriate concentration into the olefinic hydrocarbon feedstock to be polymerized and then subjecting such a dispersion to polymerization.
21. A process according to Claim 12 wherein olefinic hydrocarbon is
- 30 used for alkylation of paraffins, isoparaffins or aromatics to form alkylates.
22. A process according to Claim 21 wherein the alkylation reaction is that of alkylating aromatics and is carried out at a temperature of eg below 100°C, suitably from -30 to +50°C.
- 35 23. A process according to Claim 21 or 22 wherein the mole ratio of

the ionic liquid to the olefinic hydrocarbon used for alkylation is in the range from 1000 : 1 to 1 : 1000.

24. A process according to any one of the preceding Claims 21-23 wherein the aromatic hydrocarbon alkylated is benzene or toluene.

5 25. A process according to Claim 21 wherein during the alkylation of an iso-paraffin, the mole ratio of iso-paraffins to olefin is in the range from 1000 : 1 to 1 : 1000.

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INTERNATIONAL SEARCH REPORT

Inter: nal Application No
PCT/GB 95/00252

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F4/00 C07C2/54 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 558 187 (BP CHEMICALS LTD.) 1 September 1993 see page 3, line 12 - line 21; claims 1-10 ---	1,8,10, 12,20
A	FR,A,2 611 700 (INSTITUT FRANCAIS DU PETROLE) 9 September 1988 cited in the application see page 2, line 29 - line 31; claims 1-10 ---	1,10,12
A	FR,A,2 626 572 (INSTITUT FRANCAIS DU PETROLE) 4 August 1989 cited in the application see page 3, line 22 - line 29; claims 1-6 ---	1,8,10, 12
A	GB,A,2 024 805 (TH. GOLDSCHMIDT AG) 16 January 1980 see claims 1-3 -----	1,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 95/00252

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